

THE EXCHANGEABLE CATION STATUS
OF SOME WEST CENTRAL ALBERTA SOILS

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ABSTRACT

The object of this study was to determine whether or not a relationship exists between the exchangeable cation status of the soil and the amount of podzolic degradation that has taken place in soils of west central Alberta. Twenty-two profiles representing eight series were used. Methods of analysis were selected and developed to combine speed and accuracy.

In addition to the determination of the exchangeable cations other determinations which were thought to be significant in this study were also carried out. The results show that a striking relationship does exist between the amount of degradation that has occurred and the exchangeable cations in these soils. The exchangeable calcium decreases while exchangeable hydrogen increases as degradation proceeds. Exchangeable sodium and magnesium increase slightly while exchangeable potassium increases considerably in the horizons of eluviation. The clay content of the soils was found to be related to the percentage Al_2O_3 in total fusion analysis and to the total cation exchange capacity. The analytical data clearly justify the field classification of the soil series studied with one exception. This exception, a so-called mountain podzol, possesses morphological features similar to a podzol, but the analytical data in no way justify its classification as a podzolic soil.



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THE EXCHANGEABLE CATION STATUS
OF SOME WEST CENTRAL ALBERTA SOILS

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY OF AGRICULTURE
DEPARTMENT OF SOILS

by

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THE EXCHANGEABLE CATION STATUS
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INTRODUCTION

The importance of cation exchange was first realized in the eighteenth and nineteenth centuries and was related to purification of water with sand (13). Later cation exchange properties were related to many phenomena in the soil.

Kelley (13) mentions that Sir Daniel Hall at Rothamstead realized that good soils have large amounts of exchangeable cations and that cation exchange was a better clue to fertility than any other previously used chemical property of soil. Kelley (13) has stated that soils having large amounts of exchangeable calcium are fertile whereas soils high in exchangeable magnesium are infertile. He also stated that if hydrogen constitutes an excessive part of the exchange complex the soil is likely to be deficient in calcium. Gedroiz and Weigner (10, 40) were among the first to observe that the physical properties of soil are affected by the kinds and proportions of exchangeable cations. They stated that if calcium is the predominant replaceable cation, the clay particles assume the form of aggregates while the presence of appreciable proportions of sodium ions on the exchange complex results in highly dispersed soils. They suggest that with hydrogen domination of the exchange complex flocculation of the soil will be between these conditions.

The study of cation exchange brought new concepts in soil classification. The exchangeable ions on the exchange complex greatly determine the properties and characteristics of soils, especially of the clay fraction. Clay in turn imparts to the soil morphological features and characteristics which are recognizable in the field and which characterize the various soil horizons. Soils of different great soil groups having obvious profile differences should have these differences reflected in amounts and proportions of exchangeable cations in the various horizons of their profiles.

This study was undertaken to determine the exchangeable cation status of some Alberta soils with a view to correlating the cation exchange characteristics with morphological features of the profiles. The study is concerned with soils which represent successive stages of soil degradation progressing from a normal black earth profile to a podzolized grey wooded profile in west central Alberta. The soil series studied are developed on the same or closely related parent materials.

In addition to exchangeable cation determinations, some other analyses were made. The mechanical fractions and the pH values of all the sampled soil horizons were also determined. Total silicate analyses were conducted on several of the soil samples in order to determine whether or not a relationship exists between the various cation constituents of the soil and the type of cation adsorbed on the exchange complex. The carbon and nitrogen content, and the volume weights of various sampled horizons were determined in order

to obtain information concerning organic matter content, fertility, and compaction of these horizons.

REVIEW OF LITERATURE

Part I Relationship of Cation Exchange to Soil Degradation

The changing of a normal black soil to a podzol involves a striking change in the cation status of the soil (10, 39). Gedroiz (10) proposed a definite sequence when soils change from chernozems to podzols. He first described chernozem as a dark soil having the cation exchange complex saturated with metallic cations, mostly calcium and magnesium. The sodium and potassium which were originally present in the mother rock having been easily weathered and highly soluble, were soon leached to lower horizons. As a result where the ground water level is relatively deep, sodium and potassium are almost absent from the exchange complex of the upper horizons. Gedroiz suggested that since calcium and magnesium salts are less soluble than sodium and potassium they exist at such a level in the soil profile that they may be brought to the surface with the rise of soil moisture. He said that since calcium has the highest concentration in the soil moisture it would have the greatest replacement power and would dominate the exchange complex. He stated that chernozems are normally calcium dominated and as a result exhibit a special resistance to dissolving action and decomposition by water.

Gedroiz further described a chernozem as a soil with no compact illuvial horizons, being well flocculated and normally having good aggregation.

Under somewhat more humid conditions than those where chernozems develop Gedroiz proposed that there is a sequence of changes which he outlined as follows. First there is a tree invasion of what was formerly a grassland soil. The increase in humidity causes the lime layer in the chernozem to be leached downward and out of the profile. Eventually a point is reached when calcium is no longer returned to the surface soil horizons by capillary rise of soil moisture. This results in the calcium and magnesium concentration being greatly reduced in the soil moisture near the surface. In addition the soil moisture becomes slightly acidic from carbon-dioxide of the air dissolved in rainwater and from the breakdown of organic matter on the soil surface. These hydrogen ions in the soil moisture are able to compete more favourably with calcium and magnesium for positions on the exchange complex. Gedroiz described a leached chernozem as a soil in which the calcium and magnesium are beginning to be replaced by hydrogen ions on the exchange complex. As the process of replacement continues the soil exchange complex becomes less saturated with metallic cations and more saturated with hydrogen ions. This results in the formation of a degraded chernozem. Gedroiz believed that the stability of the exchange complex depends upon the nature of the adsorbed cations and that exchange complexes dominated by exchangeable hydrogen dissolve

more readily than those containing calcium and magnesium. He believed that the leaf litter on the surface of the soil decomposes rapidly under these conditions resulting in the process of podzolization. The hydrogen saturated aluminosilicates near the surface of the soil break down into their individual oxides. Since these oxides are fairly soluble under acidic conditions they leach downward in the soil. After being washed down to a more alkaline region they are precipitated because of their relative insolubility under these conditions. As a result of its insolubility in an acid medium silica is left in the upper eluvial layer which has been designated as the A₂ horizon. Due to the removal of clay from the A₂, by its breakdown, the cation exchange capacity there decreases and the exchange complex becomes progressively more nearly saturated with hydrogen ions. An active reformation of illuvial humus present takes place immediately below the horizon of eluviation. This horizon has the highest concentration of exchangeable hydrogen in the soil. The deposition of iron and aluminum oxides takes place immediately below this humic horizon to form what is known as the B₂ horizon. Horizons of illuviation have large exchange capacities and are largely saturated with calcium and magnesium ions. The end result of these changes outlined by Gedroiz is a well leached platy eluvial horizon and a firm compact illuvial horizon.

However since the time of Gedroiz' paper newer ideas have replaced many of his explanations outlined in the foregoing discussion. The relatively stable conditions found in

chernozems were described in Soils and Men (39) as follows. Circulation of cations from the decomposition of roots and vegetative growth on the surface, keeps the profile near a neutral pH and the soil exchange complex continues to be dominated by these cations. Under these conditions alumino-silicate clays are stable and little weathered. There is little disruption of clay and so little texture differentiation of the profile.

Under the somewhat moister conditions prevailing with tree cover the foregoing conditions change and thus important effects on the soil result. There is an increase in the amount of new organic matter now falling to the soil and decomposition proceeds to near completion with the result that more carbonic acid and other acidic compounds are formed. Some of the organic matter accumulated in the A₁ of a chernozem is also decomposed. Now with reduced circulation of bases due to tree vegetation and with greater depth of water penetration, there is a tendency to leach the lime layer deeper. There is also a tendency to change the proportions of exchangeable cations in the horizons above the lime layer. The soil moisture near the surface is now slightly acidic.

Until quite recently it was believed that the hydrogen ions in the slightly acidic soil moisture replaced calcium and magnesium on the exchange complex in the upper soil horizons. However several workers (7) have shown that under slightly acidic conditions the clays present in the A horizon

actually break down very slowly with the liberation of ionic aluminum. Since this ionic aluminum has a very high replacement power, they believe that this aluminum replaces a large proportion of the other cations on the exchange complex. As yet no generally used method for determination of exchangeable aluminum is available. It is therefore still uncertain whether aluminum does in fact occupy a significant proportion of the exchange complex in eluviated horizons.

It is generally agreed that there is some movement of clays from the upper eluvial horizons to lower regions. This has been explained by two conflicting theories: One theory proposes a physical translocation of colloidal material (39). This presupposes a peptizing action producing a colloidal suspension which moves through the pore spaces in the soil. The second theory suggests a chemical breakdown of the silicate clays with the production of some soluble materials which move in solution and are then subsequently reprecipitated in a lower horizon (31). McCaleb¹ believes three processes are responsible for the clay accumulation in the horizon of illuviation: physical translocation, inheritance from the parent rock, and destruction and resynthesis. As yet data intended to prove his proposals are unpublished.

As a result of clay removal from the A₂ this horizon is left with a lowered total cation exchange capacity. The

¹personal communication

such determinations.

Among the problems confronting soil scientists, was the preparation of an extracting solution for cation exchange determinations. It was desired to have an extracting solution which would not interfere with subsequent determinations and which at the same time would readily replace the adsorbed cations on the exchange complex. One of the earliest workers who studied exchangeable cation replacement was Hissink (11). Hissink used an unbuffered ammonium chloride solution for removing exchangeable cations from the soil, because he believed that the extracting solution should have the same pH as the soil. However Kelley and Brown (14) have found it necessary to neutralize the ammonium chloride to a pH of seven with ammonium hydroxide. This was necessary for the complete replacement of the exchangeable cations by ammonia. Otherwise the exchangeable cations would have been replaced both by hydrogen and ammonia when the soils concerned were acidic. With unbuffered ammonium chloride a determination of the total exchange capacity by determining the adsorbed ammonia in the leached soil, would have given results that were low. Kelley (13) has discussed buffered salt solutions such as barium chloride which have been used for extracting exchangeable cations. He concluded that these solutions were not satisfactory since the total exchange capacity must be determined on a separate soil sample. Acids have not been found useful for the removal of exchangeable cations from the soil because of their great dissolving power.

At present ammonium acetate is most widely used for extracting exchangeable cations from the soil. The advantages of using ammonium acetate as listed by Schollenberger and Dreibebis (32) may be summed up as follows:

- (1) It is strongly buffered at a pH of seven.
- (2) The same soil sample can be used for the determinations of the total exchange capacity and the exchange cations present.
- (3) Ammonium acetate is easily expelled from the leachate by evaporation.
- (4) Ammonium acetate is soluble in alcohol which facilitates the removal of the excess ammonium acetate after leaching.
- (5) It is inexpensive in a relatively pure form.
- (6) Ammonium acetate can better replace hydrogen ions since the hydrogen ion concentration is not increased to any considerable extent by the accumulated products of the exchange reaction.

Further advantages reported by Wynnyk (42) are:

- (1) It is possible to determine exchangeable hydrogen on the same extract.
- (2) It is widely used and serves as a better basis for comparison.

A disadvantage of ammonium acetate is that the exchangeable cations removed from the exchange complex by ammonium ions at a pH of seven vary from the amount that would be removed if the solution assumed the same pH as the soil which is leached.

Because of its many advantages ammonium

acetate was used for the replacement of the exchangeable cations adsorbed on the soil exchange complexes in this work.

Various leaching procedures have been used in order to replace the exchangeable cations present on the exchange complex. Schollenberger and Driebelbis (32) used a closed system of leaching to minimize excessive evaporation and contamination. Bentley (3) reported the use of filter mats on Buchner funnels. The Buchners were fitted on suction flasks and suction was applied. The closed system of leaching and the Buchner method were compared by Wynnyk (42). The Buchner method was found to be quicker and more practical since it was facilitated by suction. Recently several research workers have reported the digestion of the soil for a period of several hours (9, 25) prior to actual leaching in order that complete replacement may take place.

The method used here was a combination of the best of the more convenient procedures.

When the cation exchange capacity is found by determining the ammonium adsorbed on the exchange complex, excess ammonium acetate present must be removed from the soil. This has been done in several ways. In the earlier part of the century water was used for removing the excess leaching solution. With this procedure there was considerable loss of replaceable ammonia through hydrolysis. Kelley and Brown (14) used methyl alcohol for washing the ammonia saturated soils. They were unsuccessful in removing all ammonium ions by this procedure for the alcohol coagulated the colloidal material

and prevented further washing. In addition methyl alcohol was unsatisfactory for it contains separable esters, organic acids and organic compounds as impurities. For ammonia removal Schollenberger and Dreibelbis (32) used 80% ethanol which was adjusted to a pH of seven. However they found that a considerable amount of adsorbed ammonia was removed in the washings due to the water present. In 1940 the association of Official Agricultural Chemists recommended the use of 95% ethanol. The alcohol was not neutralized. Shaw (33) compared neutralized and un-neutralized ethanol, and found a slightly higher value for the total cation exchange capacity in the soil which was washed with neutralized ethanol. This was attributed to the slight amount of ammonia in the alcohol remaining in the soil after leaching. Peech (25) found it best to avoid neutralization of the ethanol providing that a proper test does not disclose the presence of large amounts of acid. Such tests are best conducted on dilute alcohol solutions because ionization is much lower in 95% alcohol. It was decided to follow Peech's method for removal of excess ammonium acetate from the leached soils.

Since it was decided to use ammonium acetate for replacing cations on the exchange complex the different methods for the determination of total exchange capacity depend upon the determination of the ammonium ions which replaced the cations on the exchange complex. Kelley (13) determined the amount of ammonia in the leached soil by aeration, after the addition of 200 cc. of 5% sodium carbonate. The ammonia was

collected in a standard acid solution. A vacuum was used to aid aeration. However this method required too long a period of time for complete recovery of ammonia. Wynnyk (42) carried out distillation directly on the leached soil and collected the distillate in a standard acid solution. He reported that in many cases excessive foaming hindered distillation. The method used by Peech (25) was one in which the exchangeable ammonia was brought back into solution by carrying out a second leaching with 10% NaCl. The sodium replaced the ammonium ion on the exchange complex. Then ammonia was determined by distillation of a portion of the leachate. Ammonia was also determined in the leachate by nesslerization. The nesslerization method was quite rapid once a standard curve was established. However this procedure may be interfered with by ammonia fumes in the laboratory.

It was therefore decided to carry out the total exchange capacity determination by the distillation of a portion of the sodium chloride leachate.

Several methods have been used for the determination of exchangeable hydrogen. The differential method as outlined by Kelley (13) depends on the determination of the difference between the total exchange capacity and the amount of exchangeable metallic cations present. Errors in this method may arise from several sources. It is difficult to accurately determine the replaceable cations in the soil. Also trivalent cations of neutral salts present may come into solution as a result of cation exchange or solvent action of acids formed

between the soil and neutral salts. As a result the sum of the exchangeable cations would become higher and the exchangeable hydrogen ion concentration would become correspondingly lower. Pierre (26) determined exchangeable hydrogen by titrating the soil with $\text{Ba}(\text{OH})_2$ to a pH of 7. However it required from 2 to 3 days for equilibrium to be reached. This made the procedure rather drawn out. This method did compare favourably with other methods for determining exchangeable H in the soil. Parker (24) outlined the use of barium acetate for determining exchangeable hydrogen. The soil is leached with barium acetate adjusted to a pH of seven. The leachate is then titrated with 0.1N $\text{Ba}(\text{OH})_2$ to a pH of seven. The endpoint was determined electrometrically using a hydrogen electrode. The disadvantage of this method is that it requires a separate leaching of the soil for the determination of exchangeable hydrogen. The determination of other exchangeable cations present in the soil necessitates the leaching of a second portion of the soil.

Parker (24) tried to determine the exchangeable hydrogen in the soil by carrying out a conductometric titration between the soil and a base. He followed two separate procedures. Given quantities of soil were placed in volumetrics and varying quantities of base were added. After a short interval of time the conductivity was measured while the solutions were titrated with $\text{Ba}(\text{OH})_2$. However no definite endpoints could be obtained. In the second procedure varying amounts of soil were added to a given quantity of base. The conductivity was measured as the soil was being added. A definite end point was obtained.

This was probably due to the absorption of the base by the added soil.

Schollenberger and Dreibelbis (32) determined exchangeable hydrogen directly on the ammonium acetate leachate used for determining the exchangeable cations. A portion of the extract was titrated with 2N NH_4OH using a potentiometer to determine the end point. Brown (5) followed a method similar to that of Dreibelbis and Schollenberger. Instead of titrating the solution to measure the acidity, he determined the change in pH which took place in the solution during leaching and used this as a measure of the hydrogen replaced on the exchange complex in the soil. Because of its rapidity a method similar to that of Brown's was used for determining exchangeable hydrogen in this study.

The methods followed for preparing the ammonium acetate leachate for metallic cation analyses and the methods for determining these cations have varied considerably in the past. The cations which were usually determined were sodium, potassium, calcium and magnesium. Schollenberger and Dreibelbis (32) were only concerned with the removal of soluble organic matter from the leachates before determining the exchangeable cations. The determinations carried out involved the use of gravimetric and volumetric methods of analyses. Such methods generally require a considerable amount of time when working with a large number of samples. This is especially true for the determination of sodium and potassium.

Recently the spectrophotometer and the flame photometer have provided more convenient methods for many of these analyses. Several workers (9, 25) have found it necessary to remove all interfering ions and any material in suspension present in the leachate before flame photometric analyses. Fieldes et al (9) used the flame photometer for analyses of sodium, calcium, magnesium, and potassium and removed many extraneous materials. The advantage of using the flame photometer is that all analyses can be carried out on the one solution. The disadvantage is that these cations are all present in the same solution and may interfere with each other. However this difficulty has been overcome by the addition of the interfering cations to the extent where a further addition no longer produces any affect upon the determination of any other cation. Because of its rapidity this method was used for determining the exchangeable sodium and potassium.

In view of the fact that exchangeable cation determinations must be carried out on a large number of soil samples, the methods were chosen to facilitate rapid determinations and yet maintain a satisfactory degree of accuracy.

MATERIALS AND METHODS

Materials

The confidence placed in analytical data depends largely upon the sampling procedures followed. For this study individual horizons were sampled from profiles which were typical of the soil series and the surrounding area.

These profiles showed a progressive degradation from a normal black earth profile to a podzolized grey wooded profile. An additional profile, not related to this sequence, was also sampled. This latter profile, a mountain podzol, exhibited a characteristic uncommon to podzols, in that it had an alkaline pH in all horizons. The name mountain podzol was used for want of a better name. The samples were gathered from the general area lying between Gull Lake, Innisfail, and west to the Rocky Mountains. All soils, with the exception of the mountain podzol have similar parent materials.

Descriptions of the soil profiles sampled are outlined in Table 1, P.20-21 and the descriptions of the soil series follow.

Antler Loam

The Antler series has a black earth profile and is developed on glacial till derived from the Paskapoo geological formation. The parent material is high in lime and contains sandstone erratics. The topography of the Antler soil is undulating to hilly with good drainage. It is found under a mixed parkland vegetation of grass, shrubs and poplar trees.

Cygnets Loam

The Cygnets series has a solodic profile developed on glacial till derived from the Paskapoo formation. The parent material is similar to that of the Antler. Since Cygnets soil represents the range from an Antler to a degraded black soil, an incipient A₂ may be present. However no A₂ was present

in the Cygnet profiles used for this study. The topography of the Cygnet soil is undulating to hilly with good drainage. The vegetative cover is chiefly grass, shrubs and poplar trees.

Falun Loam

The Falun series has a black earth profile with degradation in the A horizon. The parent material is glacial till derived largely from the Paskapoo formation. However, it lies close to the contact line between the Edmonton and the Paskapoo formation and may contain some Edmonton formation material. The topography of Falun soils is undulating to gently rolling with good drainage. The predominant vegetative cover is aspen poplar and balsam poplar along with grass and shrubs.

Benalto Loam

The Benalto series has a black earth profile showing degradation in the A horizon and is developed on glacial till derived from the Paskapoo geological formation. The topography of the Benalto soil is undulating to gently rolling, the drainage is good, and the soil has a dominant vegetative cover of aspen poplar and willow. The Benalto series differs from the Falun largely in the type of till from which it was derived.

Breton Loam

The Breton series has a grey wooded profile and is developed on till derived from the Paskapoo formation. The

parent material is quite often highly silicious. The Breton soil is found in well drained positions. The topography is of an undulating to rolling morainal type. The vegetative cover is largely aspen poplar with some balsam poplar and spruce.

Caroline Silt Loam

The Caroline series has a podzolized grey wooded profile developed on lacustrine parent material underlain by till derived largely from the Paskapoo formation. Quite often till occurs within 30 inches from the surface. The forest cover is primarily of white poplar and lodge pole pine. The topography is undulating with good drainage.

Lobley Loam

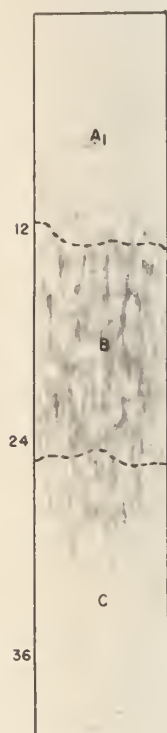
The Lobley series has a podzolized grey wooded profile developed on glacial till deposited during the Cordilleran glaciation. The Lobley soil is found in well drained positions on undulating to rolling topography. The area has a forest vegetative cover consisting of lodge pole pine and a few shrubs.

Mountain Podzol

The mountain podzol profile used in this study is developed on colluvial parent material. Bedrock occurs at about forty inches. The soil is found in well drained positions on a mountainous topography. The dominant vegetation is lodge pole pine. This mountain podzol lacks the acidity present in the upper horizons of other podzols. As yet this soil has not been named as a separate series nor found in extensive areas.

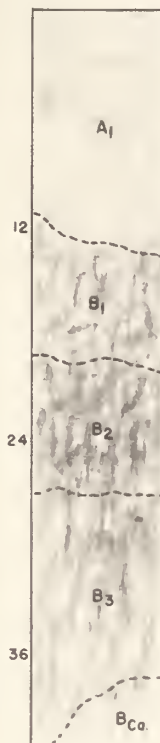
TABLE 1 Profile characteristics of some west central Alberta soils

Antler loam



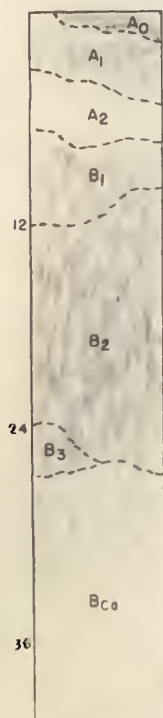
Dominant texture	Color	Dominant structure
Loam	Black	Loose friable
Loam to clay loam	Yellowish brown	Prismatic with a nuciform mesostructure
Clay loam	Brownish olive	Friable till

Cygnat loam



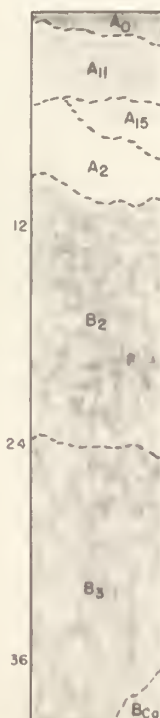
Dominant texture	Color	Dominant structure
Loam	Black	Loose granular
Loam to clay loam	Brown to greyish brown	Firm, small nuciform mesostructure
Clay loam	Yellowish brown	Mildly columnar medium nuciform
Clay loam	Dark yellowish brown	Less firm than the B ₂
Loam to clay loam	Brownish olive	Massive to large nuciform

Falun loam



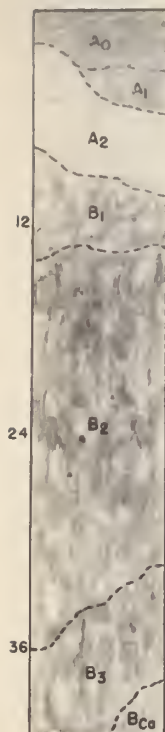
Dominant texture	Color	Dominant structure
		Leaf mold
Silt loam	Black	Loose granular weakly platy
Silt loam	Light brown grey	Platy to fragmental
Loam-clay loam	Yellowish brown	Friable blocky
Clay loam	Dark yellowish brown	Blocky to nuciform
Loam	Light olive	Massive to blocky

Benalto loam



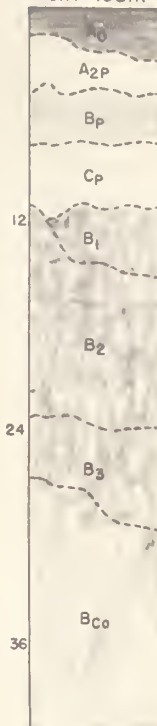
Dominant texture	Color	Dominant structure
		Grass and leaf mold
Silt loam	Black	Loose to small granular
Silt loam	Dark yellowish brown	Granular to weakly platy
Silt loam	Dark greyish brown	Medium to coarse platy
Clay loam	Dark yellowish brown	Medium nuciform
Loam to clay loam	Yellowish brown	Medium to large nuciform
Loam to clay loam	Dark yellowish brown	Blocky

Breton loam



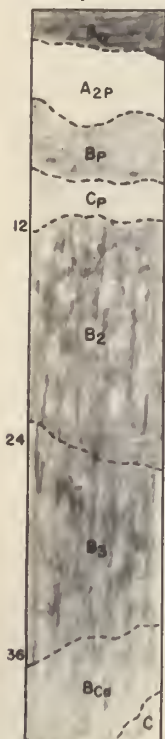
Dominant texture	Color	Dominant structure
		Leaf mat
Silt loam	Dark brown	Loose
Sandy loam	Greyish brown	Platy
Clay loam	Dark yellowish brown	Transition to B2
Clay loam	Dark yellowish brown	Medium nuciform to blocky
Clay loam	Dark yellowish brown	Medium nuciform less defined than the B2
Clay loam	Dark yellowish brown	Blocky

Caroline* silt loam



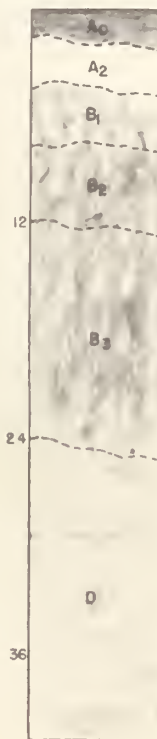
Dominant texture	Color	Dominant structure
		Leaf mat
Silt loam	Pinkish grey	Fine platy to single grain
Silt loam	Strong brown	Fine platy to crumb
Silt loam	Light brownish grey	Medium to coarse platy
Silty clay loam to clay loam	Dark brown	Nuciform to granular
Silty clay loam to silty clay	Dark brown to dark yellowish brown	Fine to medium nuciform
Clay loam to silty clay	Light olive	Nuciform to massive
Clay loam to silty clay loam	Light olive	Blocky

Lobley loam*



Dominant texture	Color	Dominant structure
		Leaf mat
Silt loam	Pinkish grey	Loose
Silt loam	Yellowish brown	Crumb
Silt loam	Light brownish grey	Platy
Clay loam	Dark brown	Nuciform to blocky
Clay loam	Dark brown	Large nuciform to blocky
Loam to clay loam	Light olive	Blocky
Sandy clay loam	Light olive	Massive

Mountain podzol



Dominant texture	Color	Dominant structure
		Leaf mat
Silt loam	Greyish brown	Loose somewhat platy
Silt loam	Dark brown	weakly platy
Silt loam	Dark brown	Friable nuciform
Silt loam	Dark greyish brown	nuciform
		Bedrock shale

*The designations A_{2p}, B_p and C_p represent horizons of micro podzols found in the A horizon of a grey wooded profile. Color designations are those of the Munsell charts (22) taken for wet soils.

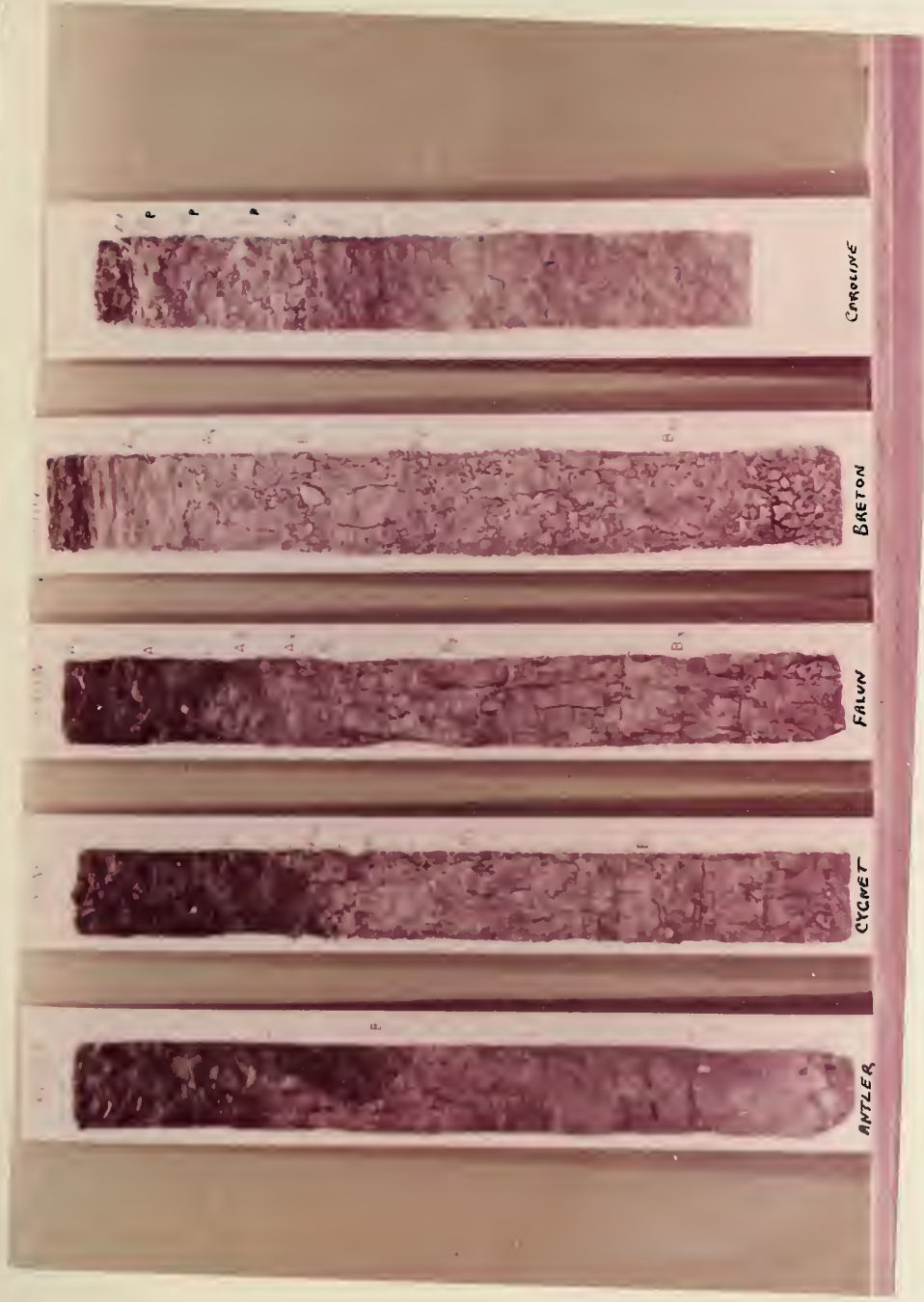


PLATE I. PROFILE CHARACTERISTICS OF SOME WEST CENTRAL ALBERTA SOILS

(These are five of the eight series concerned in this study and from left to right illustrate the progressive changes proceeding from black to podzolized grey wooded areas).

The soil samples from the individual horizons were collected in canvas bags. After they were taken to the laboratory, these samples were dried, passed through a 4-m.m. mesh sieve and stored in quart sealers. The samples, when required for analyses, were obtained from the sealers by "quartering". A 200 gm. portion of the sample was retained and passed through a 2 m.m. mesh sieve. These samples were well mixed before taking the samples for analyses.

Methods

Cation Exchange Analysis

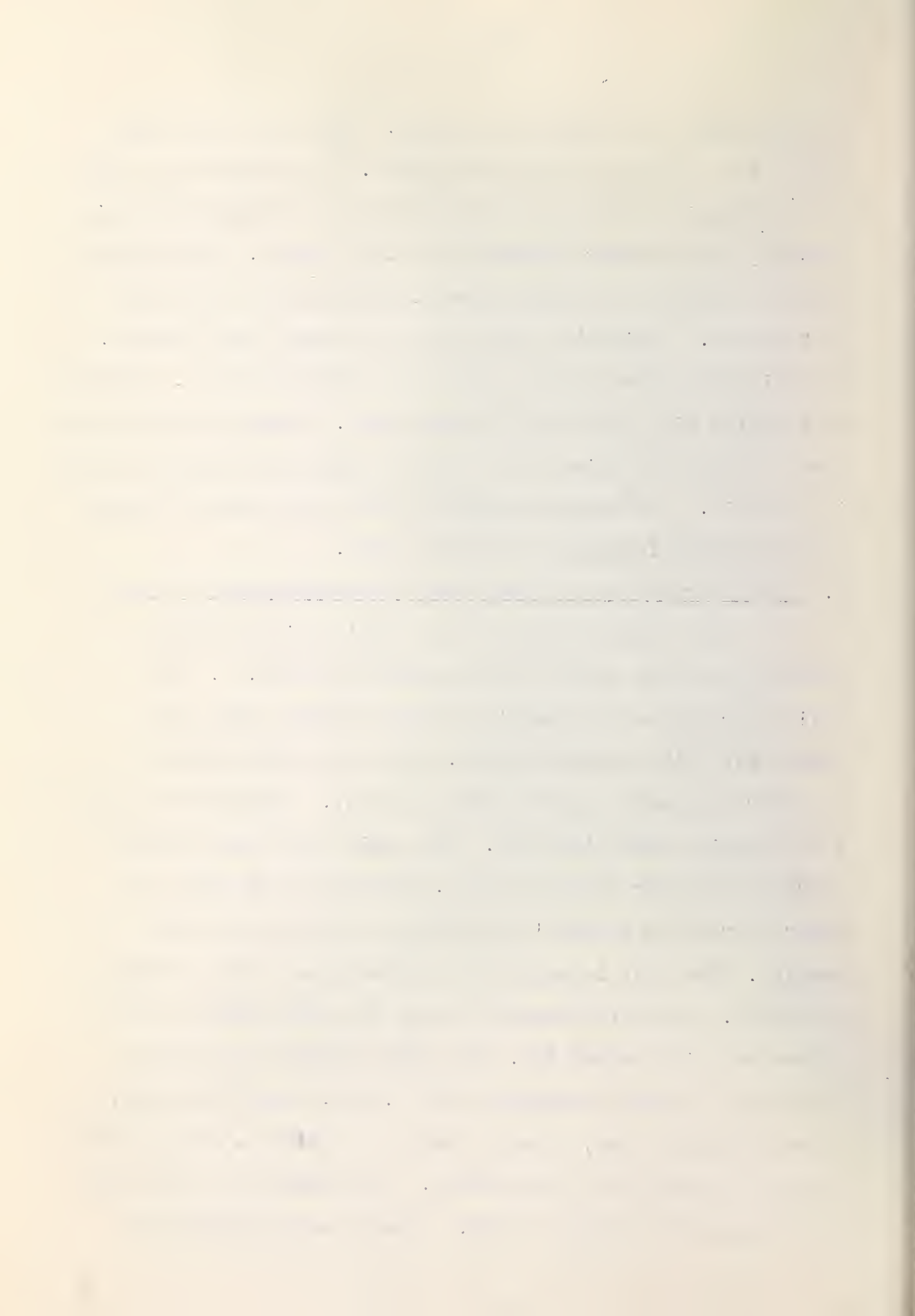
A. The Extraction of Exchangeable Cations from the Soil

Exchangeable cations were removed from the soil by the following procedure. A leaching solution of 1N NH_4Ac was prepared from a 5N NH_4Ac stock solution, and adjusted to a pH of 7.05 with either NH_4OH or H Ac depending upon the original pH of the solution. A 50 ml. portion of this leaching solution and a 6 cm. Whatman No. 1 filter paper were placed in individual 100 ml. centrifuge tubes, and stirred with a mixing machine until the filter paper was broken up into a fine fibrous mass. Ten gram samples of each of the soils to be analyzed, were taken. These samples were arranged during the analysis in groups of eight in such a manner that the identity of the profile or horizon was unknown. The samples were transferred quantitatively to the centrifuge tubes. These tubes were then stoppered, shaken for one minute, and allowed

to stand until the following morning. The tubes were then placed in a shaker for fifteen minutes. The contents of each of the centrifuge tubes were transferred quantitatively with washing, into Buchners mounted on filter flasks. The Buchner filters consisted of filter paper covered with a thin layer of "celite". Aspiration was applied to remove the leachant. The soils were then washed with four successive 50 ml. portions of 1N NH_4Ac with aspiration between each. These leachates were saved for the determination of the exchangeable cations present in the soil. The Buchners and the soils were used for cation exchange determination as outlined below.

B. The Determination of the Total Cation Exchange Capacity

The determination of the total cation exchange capacity was made on the soils prepared in Sect. A. The NH_4^+ saturated soils remaining in the Buchners were each washed with five separate 40 ml. portions of 95% ethanol in order to remove any free NH_4Ac present. The leachates in the foregoing were discarded. The soils were then leached further with four separate 50 ml. portions of 1N NaCl , in order to replace the NH_4^+ adsorbed on the soil exchange complex. The NaCl leachates were made up to a final volume of 250 ml. and their ammonia content was determined by the magnesium oxide method (2). For this analysis an aliquot of each of the NaCl leachates with 5.0 gm. magnesium oxide, a few grains of zinc, a small amount of paraffin, and H_2O were boiled to distill off the ammonia. The ammonia was recovered in 4% boric acid solution (28). Ammonia was determined by



titrating with standardized H_2SO_4 .

C. Preparation of the Soil Extract Solutions for the Determination of the Exchangeable Metallic Cations Present in the Soils

The method used for the preparation of the soil extract solutions for determinations of exchangeable Ca, Mg, Na, and K was similar to that of Fieldes et al (9).

The procedure is outlined as follows:

1. Evaporate the NH_4Ac leachate almost to dryness.
2. Transfer to 100 ml. beakers and evaporate to dryness.
3. Heat in the muffle for thirty minutes at 550°C . Take up in 20 ml. of 0.2N HCl .
4. Digest for thirty minutes on a hot plate (60°C - 90°C).
5. Titrate until neutral with standard NH_4OH using methyl red indicator.
6. Add one drop of FeCl_3 to precipitate any phosphate; 1 ml. of 1:1 NH_4OH and 2 ml. of saturated bromine water.
7. Boil for two minutes keeping alkaline with 1:1 NH_4OH .
8. Filter off residue of Fe, PO_4 , Al and Mn.
9. Evaporate to approximately 10 ml. and add 5 ml. of conc. HNO_3 .
10. Evaporate to dryness to destroy all ammonia.
11. Take up in 5 ml. of 1:1 HCl and evaporate to dryness again.
12. Add 50 ml. of 0.2 N HCl .
13. Filter by suction through a Whatman No. 42 filter paper on a sintered glass filter.
14. Save the solution for the determination of exchangeable Na, K, Ca, and Mg (add 1 drop of toluene to prevent mold).

D. The Determination of Exchangeable Hydrogen in the Soil

A modification of Brown's method (5) was used for

the determination of exchangeable hydrogen in the soil. The purpose of this modification was to reduce the buffering power of NH_4Ac by dilution. This results in greater pH changes in the extract per m.e. of exchangeable H in the soil.

The method used for the determination of exchangeable H is outlined as follows. Ten gram samples of each of the soils were weighed out on a torsion balance and digested with exactly 50 ml. of 1N NH_4Ac in 100 ml. centrifuge tubes for a period of five hours. These tubes were shaken for fifteen minutes, then centrifuged at 1000 r.p.m. for a period of five minutes. Ten milliliter portions of the supernatant liquids were transferred with a pipette to corresponding 50 ml. volumetrics, which were then made up to volume with distilled water. The pHs of these solutions were measured with a Beckman Model "N₂" pH meter. The differences in the pHs were determined by subtracting these readings from that of a blank treated similarly. The number of m.e. of H ions present were determined from a standard curve (Fig. 1) prepared by adding known increments of acetic acid to 0.2 N NH_4Ac .

On the basis of the results obtained from several soil samples this method was at least as accurate as Brown's (5). An advantage was that new standards did not have to be prepared every day as reported by Wynnyk (42) since slight changes in the pH of the 1N NH_4Ac caused no noticeable error in the exchangeable hydrogen found in the samples used in this study.

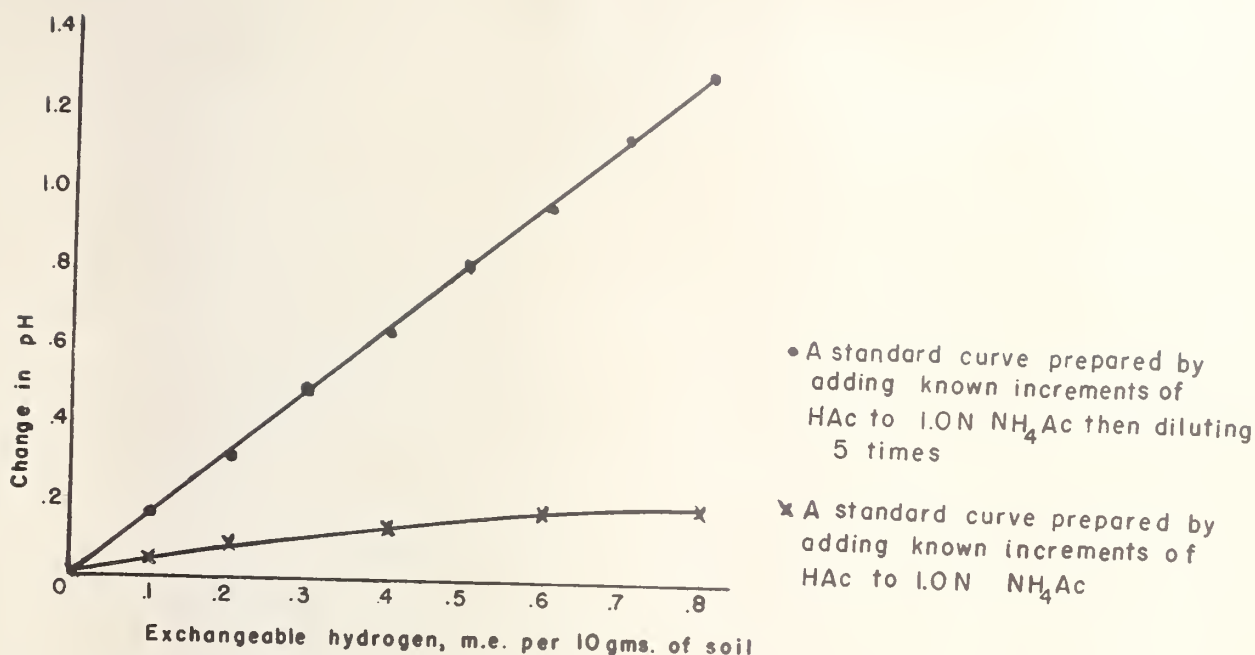


Fig.1 The relationship between exchangeable hydrogen in the soil and the change in pH of NH₄Ac extract solution before and after diluting five times

E. Determination of Exchangeable Sodium and Potassium by Flame Photometry

Flame photometry was done using a model DU Beckman quartz spectrophotometer with a model "9200" flame attachment.

A test was first carried out to determine the effect, if any, of other exchangeable cations, present in the unknown, upon the determination of Na. The results of such a test are tabulated in Table II.

TABLE II

INTERFERENCES FROM Mg, K AND Ca IN THE DETERMINATION OF Na, BY FLAME PHOTOMETRY, IN A SOLUTION CONTAINING 0.3 m.e. PER 100 ml.

Cations added to Na in m.e./100 ml.	% transmission Na solution	% transmission Na solution with additions
0.5 K	100	104
1.0 Mg	100	108
3.5 Ca	100	107.5

Table II indicates that the three cations tested interfere to some extent with the determination of sodium by the Beckman flame photometer. As a result additional determinations were carried out to test the effect of varying concentrations of K, Mg and Ca upon the percent transmission for Na. These results are tabulated in Table III.

TABLE III

THE EFFECT OF PROGRESSIVE INCREMENTS OF K, Mg AND Ca UPON THE % TRANSMISSION OF A SOLUTION CONTAINING 0.3 m.e. OF Na PER 100 ml. 0.2N WITH RESPECT TO HCl.

Calcium		Potassium		Magnesium	
m.e. added per 100 ml.	% trans- mission	m.e. added per 100 ml.	% trans- mission	m.e. added per 100 ml.	% trans- mission
0	80	0	80	0	80
1.0	82	0.5	82	0.5	81
2.0	84	1.0	82	1.0	83
3.0	86	1.5	83	1.5	83
4.0	82	2.0	80	2.0	83
5.0	82	2.5	79	2.5	83
6.0	82			3.0	82
7.0	82			3.5	81

In view of the data in Table III, a "buffer" containing 4.0 m.e. of Ca, 0.5 m.e. of K and 1.0 m.e. of Mg per 100 ml. of 0.2N HCl solution was added to the standards in the preparation of the standard curve (Fig. 2). To test the suitability of this buffer, K Ca and Mg were added to the buffered standards in the maximum concentrations expected to be encountered in the soil extract solutions. The results of this test as indicated in Fig. 2, show that the addition of these cations had no effect upon the transmission for the buffered sodium standards.

In view of the results of Fig. 2, it was necessary to add Ca, Mg, and K to the unknowns in the form of a "buffer solution" to give approximately the same concentration of these elements in the unknowns as in the standard solutions.

A recovery test was carried out in order to determine the suitability of the foregoing flame photometer method for Na determination. The results of this test are tabulated in Table IV.

TABLE IV

RECOVERY, BY FLAME PHOTOMETRY, OF Na ADDED TO
SOIL EXTRACT SOLUTIONS

<u>m.e. of Na per 100 ml. of solution</u>				
Sample No.	In soil extract	Added to test recovery	After addition	Recovered
65	.04	.03	.07	.03
65	.04	.05	.09	.05
68	.02	.03	.05	.03
68	.02	.05	.07	.05
45	.02	.03	.05	.03
45	.02	.05	.07	.05

Table IV established that the procedure described gives satisfactory accuracy for the determination of Na in this study.

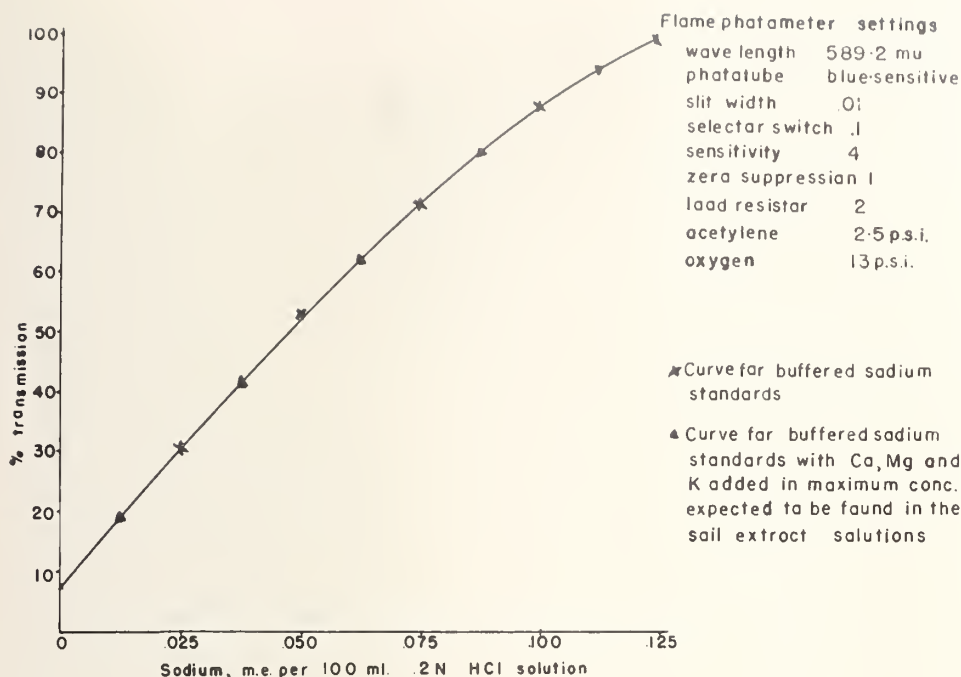


Fig.2 Determination of the effect of interfering cations upon buffered sodium standards by flame photometry

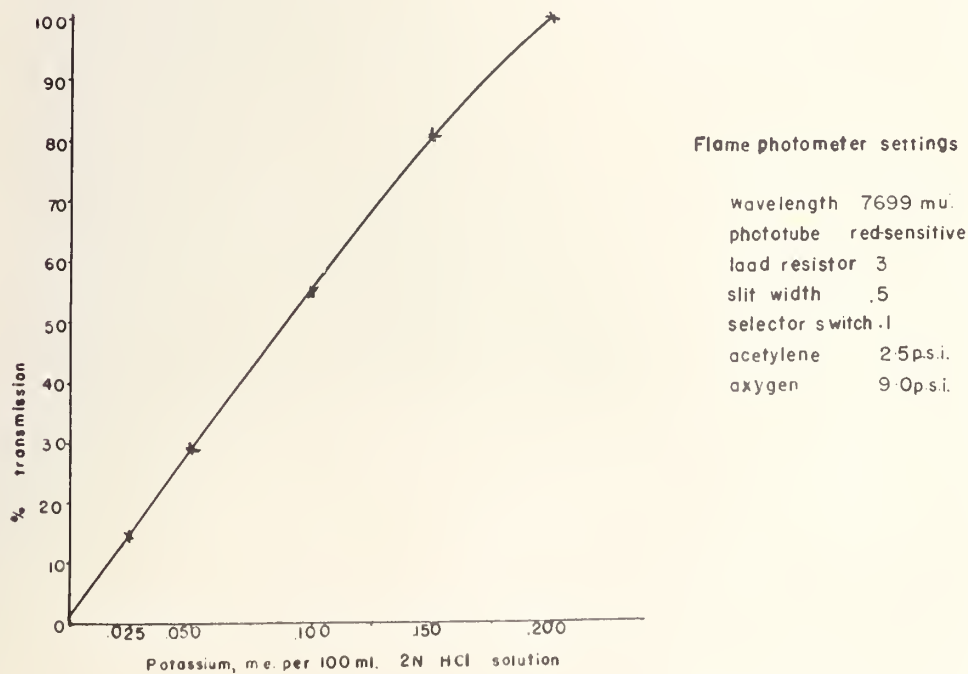


Fig3 Standard curve for exchangeable potassium determination in soils

Exchangeable potassium was also determined with the Beckman flame photometer. Tests similar to those described for Na were conducted to determine if Na, Ca or Mg interfere with the potassium determination by the flame method. No such interferences were found. Potassium was determined in unknowns from the graph shown in Fig. 3 which was prepared from standard solutions. The data of Table V are for recovery of K added to soil extract solutions and establishes the suitability of the procedure used.

TABLE V

RECOVERY, BY FLAME PHOTOMETRY, OF K ADDED TO
SOIL EXTRACT SOLUTIONS

Sample No.	<u>m.e. of K per 100 ml. of solution</u>			
	in soil extract	added to test recovery	after addition	recovered
17	.01	.02	.03	.02
17	.01	.05	.06	.05
21	.04	.02	.06	.02
21	.04	.05	.09	.05
40	.07	.02	.09	.02
40	.07	.05	.12	.05

These data in Table V establish that the flame method is suitable for the determination of K in this study.

F. Determination of Exchangeable Calcium and Magnesium

The method outlined by Bentley for the determination of exchangeable calcium and magnesium in the soil extract solutions represents a modification of the method of Cheng and Bray (6). Since this method differs widely from that outlined

by the two chemists, a detailed description is provided in sections I, A and B of the appendix.

A number of determinations (section I, C) concerning recovery tests and determinations of knowns carried out by Bentley and the author showed that this method is at least as accurate as that of Cheng and Bray. Its advantage is that any error in the determination of calcium is not included in the magnesium determination since magnesium is no longer determined by difference. Consequently determinations by this method should be more accurate than determinations by their method.

Additional Physical and Chemical Determinations

Other analyses made were done by established methods. The mechanical fractions were determined by the Modified Pipette Method outlined by Toogood (36). Total analyses were done according to the method outlined by Robinson (30). Soil pH's were determined using a Beckman Model N2 pH meter and a soil paste as described by Doughty (8). The carbon content of several of the soil samples was determined by the dry combustion process outlined by Winters (41). Nitrogen was determined by the Kjeldahl-Wilfarth-Gunning Method (2).

RESULTS

The results of the different analyses are tabulated in Tables VI (a-h), VII (a-h), VIII, IX, and X. In series VI Tables the percentages of the various exchangeable cations are based on their sums for the individual horizons. In series VII

Tables presenting averages, total cation exchange capacities are based on the direct determination by NH_3 distillation. Total fusion analyses listed in Table VIII were carried out by the soil survey laboratory staff at the University of Alberta and is not the work of the author alone.

The data in these foregoing tables suggest that there had been some disruption of clays in the upper horizons of the podzolized grey wooded profiles. It was therefore decided to determine the mechanical fractions in the upper horizons of one of these soils omitting both the peroxide and acid treatment called for in the procedure in order to determine if these treatments were affecting results. In addition the clay fractions less than 1 μ in size were collected from both treated and untreated samples. X-ray and total fusion analyses were carried out on these samples. The X-ray spectograph analyses were carried out by the Research Council of Alberta. These results are tabulated in Tables IX and X.

TABLE VI (a)

ANALYSIS OF THE ANTLER SERIES

Hori- zon	Depth in inches	pH	Mechanical Analysis			Exchangeable cations m.e./100 gm.			Total C.E.C. m.e./100 gm. by Sum. deter.			% of total C.E.C.					
			%S	%Si	%C	H	Na	K	Mg	Ca	H	Na	K	Mg	Ca		
<u>Profile I</u>																	
A	0-13	6.7	40	36	24	0.7	0.1	0.7	4.4	23.0	28.9	31.1	2	0	2	15	81
B	13-23	6.4	39	34	27	0.6	0.2	0.4	3.5	25.0	29.7	23.4	2	<1	1	12	84
C	@ 72	7.9	36	42	22	0.0	0.1	0.2	4.4	33.6	38.3	28.4	0	0	<1	12	87
<u>II</u>																	
A	0-10	6.9	40	44	16	0.6	0.2	0.4	3.7	30.3	35.2	37.0	2	<1	1	10	86
B	10-25	6.5	38	36	26	0.3	0.2	0.4	3.6	28.0	32.5	28.7	1	<1	1	11	86
C	@ 25	7.9	27	43	30	0.0	0.3	0.2	5.0	32.5	38.0	23.0	0	1	<1	13	85
<u>III</u>																	
A	0-10	6.9	31	48	21	0.7	0.2	0.5	2.7	28.8	32.9	27.7	2	<1	2	8	87
B	10-26	6.7	26	49	25	0.5	0.2	0.3	3.0	33.5	37.4	34.4	1	<1	1	8	89
C	@ 26	7.9	22	46	32	0.0	0.2	0.3	3.9	35.0	39.4	25.3	0	<1	1	10	88

TABLE VI (b)

ANALYSIS OF THE CYGNET SERIES

Hori- zon	Depth in inches	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm. by Sum. deter.				% of total C.E.C.			
		%S	%Si	%C	H	Na	K	Mg	Ca	by	H	Na	K	Mg	Ca	
Profile I																
A1	0-7	30	43	27	3.6	0.3	0.8	2.0	29.5	36.2	33.2	10	1	2	6	81
B1	7-13	32	40	28	2.7	0.4	0.6	2.7	23.8	30.2	25.3	9	1	2	9	79
B2	13-25	31	41	28	0.7	0.4	0.6	2.4	18.5	22.6	19.8	3	2	3	11	81
B3	25-34	37	31	32	0.6	0.4	0.5	3.5	18.8	23.3	22.6	3	2	2	15	78
B _{Ca}	@ 36	38	37	25	0.0	0.4	0.3	3.7	30.7	35.1	21.2	0	2	1	11	86
II																
A1	0-12	25	56	19	3.6	0.3	1.4	3.3	22.9	31.5	27.4	11	1	4	11	73
B1	12-14	31	42	27	2.5	0.3	0.3	3.4	17.7	24.2	21.1	10	1	1	14	74
B2	14-24	31	35	34	2.1	0.5	0.3	3.2	20.2	26.3	23.2	9	2	1	12	76
B3	24-54	34	32	34	1.5	0.5	0.4	3.6	19.5	25.5	22.3	6	2	2	14	76
B _{Ca}	@ 54	34	35	31	0.0	0.3	0.3	2.1	36.0	38.7	19.6	0	1	1	5	93
III																
A1	0-13	34	31	35	3.5	0.1	1.7	7.3	31.8	44.4	33.1	8	0	4	16	72
B1	13-17	38	26	36	1.0	0.2	0.4	5.7	22.2	28.5	29.5	4	1	1	20	74
B2	17-27	46	23	31	1.0	0.3	0.4	4.4	17.5	23.6	24.1	4	1	2	19	74
B3	27-32	48	22	30	0.0	0.3	0.4	5.2	17.2	23.1	20.8	0	1	2	23	74
B _{Ca}	@ 36	41	34	25	0.0	0.2	0.3	7.1	40.8	48.4	24.8	0	0	41	15	84

TABLE VI (c)

ANALYSIS OF THE FALUN SERIES

Hori- zon	Depth in inches	pH	Mechanical Analysis		Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm. by				% of total C.E.C.				
			%S	%Si	%C	H	Na	K	Mg	Ca	Sum.	deter.	H	Na	K	Mg	Ca
Profile I																	
A ₁	0-3	5.9	35	55	10	4.4	0.4	0.8	3.0	27.1	35.7	41.8	12	1	2	8	77
A ₂	3-6	5.9	36	50	14	1.6	0.2	0.3	2.0	8.9	13.0	11.2	8	2	2	15	73
B ₁	6-12	5.4	36	35	29	2.4	0.2	0.3	2.1	10.1	15.1	12.6	16	1	2	14	67
B ₂	12-24	5.2	36	35	29	2.4	0.4	0.3	2.4	15.7	21.2	20.2	14	2	1	11	72
B _{ca}	@ 48	7.6	44	38	18	0.0	0.4	0.3	3.2	21.7	25.6	17.6	0	2	1	13	84
II																	
A ₁	0-2	6.7	53	38	9	2.6	0.4	1.3	2.7	29.6	36.6	33.8	7	1	4	7	81
A ₁₅ - A ₂	2-12	6.5	57	36	7	0.7	0.2	0.2	1.0	4.4	6.5	8.5	11	3	3	15	68
B ₁	12-16	5.4	54	25	21	1.3	0.4	0.4	3.8	12.6	18.5	17.3	7	2	2	20	69
B ₂	16-32	4.9	56	16	28	2.0	0.3	0.4	5.3	13.6	21.6	20.0	9	1	2	25	63
B _{ca}	@ 48	7.5	39	48	13	0.0	0.2	0.3	4.2	15.5	20.2	14.9	0	1	2	21	76
III																	
A ₁₅ A ₁₅	1-8	5.1	31	53	16	3.6	0.4	1.3	1.7	12.0	19.0	16.8	19	2	7	9	63
A ₂	8-9	5.6	42	43	15	1.0	0.2	0.2	1.6	8.2	10.3	11.7	10	2	2	16	70
B ₂	9-36	5.2	43	31	26	1.0	0.2	0.3	3.3	12.9	17.8	24.3	6	1	2	19	72
B _{ca}	@ 36	7.8	41	36	23	0.0	0.2	0.3	4.9	27.6	33.0	24.0	0	<1	1	15	83

TABLE VI (d)

ANALYSIS OF THE BENALTO SERIES

Hori- zon	Depth in inches	pH	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm. by Sum. deter.				% of total C.E.C.			
			%S	%Si	%C	H	Na	K	Mg	Ca	Sum.	deter.	H	Na	K	Mg	Ca
Profile I																	
A ₀₀	0-2	7.1	--	--	--	1.1	0.4	1.9	2.7	30.3	36.4	49.9	3	1	5	7	84
A ₀₁ - A ₁	2-7	6.1	30	54	16	3.0	0.6	1.6	5.0	55.0	65.2	70.0	5	1	3	8	83
A ₁₅	7-11	5.8	26	52	20	2.3	0.4	0.8	1.0	13.1	17.6	16.2	13	2	5	6	74
A ₂	11-13	5.8	26	55	19	1.1	0.4	0.7	2.1	10.2	14.5	15.8	8	3	5	15	69
B ₂	13-25	5.6	29	47	24	1.4	0.4	0.6	4.1	14.0	20.5	19.9	7	2	3	20	68
B ₃	25-48	5.5	30	44	26	2.1	0.4	0.5	3.9	20.9	27.8	24.1	8	1	2	14	75
B _{ca}	@ 54	7.7	36	47	17	0.0	0.4	0.5	3.1	29.9	33.9	22.1	0	1	2	9	88
II																	
A ₁₁	3-4	6.1	26	55	19	4.4	0.5	1.1	3.8	32.8	42.6	35.4	10	1	3	9	77
A ₁₅	4-8	6.0	31	53	16	2.1	0.2	0.2	2.6	15.8	20.9	19.2	10	1	1	12	76
A ₂	8-12	5.8	33	50	17	1.4	0.2	0.2	1.7	10.8	14.3	16.6	10	1	1	12	76
B ₂	12-24	5.5	35	35	30	1.7	0.2	0.3	3.5	17.4	23.1	24.3	7	1	1	20	71
B ₃	24-54	5.3	34	39	27	1.7	0.2	0.2	3.9	20.8	26.8	24.1	6	<1	<1	15	78
B _{ca}	54†	7.2	40	33	27	0.0	0.2	0.3	1.5	30.4	32.4	20.8	0	<1	1	5	93
III																	
A ₁₁	1-4	6.1	40	41	19	3.1	0.4	1.4	3.9	38.0	46.8	44.7	7	1	3	8	81
A ₂	4-8	6.3	41	43	16	1.5	0.2	0.3	1.7	12.6	16.3	15.5	9	1	2	10	78
B ₂	8-26	5.6	44	33	23	1.9	0.2	0.5	4.4	22.7	29.7	31.7	6	<1	2	15	76
B ₃	26-72	5.2	45	29	26	2.0	0.3	0.5	3.5	21.6	29.7	24.6	7	1	2	13	77
B _{ca}	@ 72†	7.5	41	31	28	0.0	0.3	0.4	4.9	40.2	45.8	25.2	0	<1	1	11	87

TABLE VI (e)

ANALYSIS OF THE BRETON SERIES

Hori- zon	Depth in inches	pH	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm.				% of total C.E.C.			
			%S	%Si	%C	H	Na	K	Mg	Ca	Sum.	deter.	H	Na	K	Mg	Ca
Profile I																	
A ₁	3.5-4	6.5	23	55	22	3.4	0.4	1.2	5.6	54.5	65.1	58.5	5	1	2	9	83
A ₂	4-12	6.2	41	48	11	0.8	0.2	0.7	3.3	5.0	10.0	11.8	8	2	7	33	50
B ₁	12-15	5.9	38	28	34	1.0	0.2	0.8	4.6	16.4	23.0	21.0	4	1	4	20	71
B ₂	15-33	5.1	43	27	35	1.5	0.2	0.6	4.4	18.9	25.6	25.0	6	1	2	17	74
B ₃	33-80	5.3	37	28	35	1.9	0.4	0.6	3.1	15.0	21.0	19.0	9	2	3	15	71
B _{ca}	@ 84	7.6	38	34	38	0.0	0.4	0.6	3.8	27.8	32.6	20.0	0	1	2	12	85
II																	
A ₂	1.5-6	5.3	48	43	9	2.1	0.0	0.5	0.5	4.9	8.0	7.9	26	0	6	6	62
B ₁	6-10	5.2	45	31	24	1.0	0.2	0.3	3.1	15.9	20.5	26.4	5	1	2	15	77
B ₂	10-26	4.4	41	29	30	5.2	0.2	0.4	2.9	19.5	28.2	27.4	18	1	1	10	70
B ₃	26-42	5.2	36	36	28	3.1	0.2	0.3	2.5	21.9	28.0	27.6	11	1	1	9	78
B _{ca}	@ 55	7.1	33	37	30	0.0	0.4	0.6	4.8	20.7	26.5	22.2	0	1	1	7	91
III																	
A ₁	1-2	6.5	49	39	12	3.3	0.3	2.8	3.2	30.6	40.2	46.6	8	1	1	8	76
A ₂	2-8	6.9	24	68	8	2.1	0.4	0.5	0.4	5.9	9.3	5.8	23	4	5	4	64
B ₁	8-12	6.0	30	40	30	1.3	0.3	0.7	3.8	17.0	23.1	19.4	6	1	3	17	73
B ₂	12-60	5.8	34	31	32	1.2	0.2	0.7	5.3	19.5	26.9	21.8	5	1	3	20	72
B ₃	@ 72	5.5	38	41	21	0.2	0.4	0.9	4.6	21.7	27.8	21.2	1	1	3	17	78

TABLE VI (f)

ANALYSIS OF THE CAROLINE SERIES

Hori- zon	Depth in inches	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm. by				% of total C.E.C.				
		%S	%Si	%C	H	Na	K	Mg	Ca	Sum. deter.	H	Na	K	Mg	Ca		
Profile I																	
A _{2p}	2-3	5.5	26	24	10	2.5	0.2	0.5	1.9	6.8	11.9	10.7	21	2	4	16	57
B _p	3-5	5.8	24	66	10	3.7	0.2	1.4	1.0	4.4	10.7	11.8	35	2	13	9	41
C _p	5-9	5.5	26	67	7	1.1	0.1	1.3	1.3	5.7	9.5	7.1	12	1	14	14	59
B ₁	9-13	5.0	23	45	32	1.4	0.2	0.6	1.9	10.1	14.2	14.0	10	1	4	13	72
B ₂	13-20	5.0	45	27	28	1.2	0.2	0.5	1.8	14.7	18.4	15.2	7	1	3	10	79
B ₃	20-24	4.9	39	31	30	1.1	0.3	1.2	3.2	13.4	19.2	17.7	6	2	6	17	69
B _{ca}	@ 24	6.9	40	42	18	0.0	0.1	0.3	4.2	17.0	21.6	22.0	0	1	1	19	79

II

A _{2p}	1-2	5.3	26	66	8	1.9	0.1	0.3	1.6	7.2	11.1	11.9	17	1 3 14 65
B _p	2-4	5.6	23	67	10	2.9	0.2	0.8	1.0	8.5	13.4	11.7	22	2 6 8 63
C _p	4-7	5.5	19	61	10	1.8	0.1	0.5	1.8	9.3	13.5	12.4	13	1 4 13 69
B ₁	7-16	5.3	14	44	42	1.9	0.4	1.3	7.3	39.6	50.5	40.5	4	1 3 15 78
B ₂	16-24	5.4	9	36	55	3.6	0.2	0.7	5.0	25.2	34.7	32.2	10	1 2 14 73
B ₃	24-36	5.6	1	42	57	3.0	0.4	0.6	5.7	30.1	39.8	36.6	8	1 2 14 75
B _{ca}	@ 36	5.6	1	58	41	0.0	0.5	0.5	4.8	53.3	59.1	38.1	0	1 1 8 90

III

A _o	0-1	7.0	37	49	14	1.9	0.7	1.7	10.9	53.2	68.4	56.5	3	1 3 16 77
A _{2p}	1-3	6.3	25	63	12	1.7	0.3	0.4	2.1	7.5	12.0	15.7	14	3 3 18 62
B _p	3-5	6.0	20	65	15	2.6	0.5	0.8	2.4	9.4	15.7	19.1	17	3 5 15 60
C _p	5-8	5.9	17	78	5	1.1	0.4	0.2	1.3	5.4	8.4	8.3	13	5 2 16 64
B ₂	8-14	5.4	4	70	26	1.7	0.4	0.5	4.3	14.2	21.1	22.0	8	1 2 20 69
B _{ca}	@ 14	8.0	3	68	29	0.0	0.6	0.2	2.6	33.2	36.6	27.2	0	2 1 7 90

TABLE VI (g)

ANALYSIS OF THE LOBLEY SERIES

Hori- zon	Depth in inches	pH	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm. by Sum. deter.				% of total C.E.C.			
			%S	%Si	%C	H	Na	K	Mg	Ca	by	H	Na	K	Mg	Ca	
Profile I																	
A2p	3-5	4.6	42	42	16	4.0	0.4	0.1	.9	3.6	9.0	10.1	44	4	1	10	41
Bp	5-7	5.9	43	41	16	2.4	0.4	0.4	1.3	4.8	9.3	11.3	26	4	4	14	52
Cp	7-14	6.0	58	36	6	1.3	0.2	0.1	1.4	4.9	7.8	6.5	17	3	1	18	61
B2	14-30	5.2	35	26	39	2.3	0.5	0.1	3.6	14.8	21.3	20.9	11	2	1	17	69
B3	30-44	5.8	27	43	30	2.2	0.4	0.1	3.3	17.6	23.6	24.1	9	2	1	14	74
Bca	@ 44	7.7	44	41	15	0.0	0.4	0.3	3.8	32.8	37.3	19.4	0	1	1	10	88
II																	
Ao	0-2	6.8	--	--	--	2.5	0.2	0.7	6.4	43.6	53.4	54.7	5	1	1	12	81
A2p	2-3	5.6	30	62	18	2.6	0.3	1.5	0.9	4.2	9.5	11.5	37	3	16	10	34
Bp	3-7	5.0	36	57	8	4.4	0.2	0.7	2.0	6.9	14.2	14.2	31	1	5	14	49
Cp	7-12	5.7	37	62	1	2.8	0.2	0.2	1.1	4.4	8.7	8.8	32	2	2	13	51
B2	12-24	5.2	39	40	21	2.6	0.2	0.2	3.6	11.3	17.9	15.1	15	1	1	20	63
Bca	@ 36	7.7	30	44	26	0.0	0.2	0.3	5.8	34.5	40.8	20.5	0	1	1	14	85
III																	
A2p	1-2	6.2	28	65	7	1.4	0.1	0.4	1.1	6.0	9.0	7.6	16	1	4	12	67
Bp	2-3	5.5	33	54	13	3.9	0.1	0.5	1.5	8.8	14.8	13.5	26	1	3	10	60
Cp	3-4	5.4	32	60	8	2.9	0.0	0.3	1.1	5.5	9.8	7.8	30	0	3	11	56
B2	4-10	5.1	38	31	31	4.6	0.1	0.4	4.0	14.0	23.1	21.5	20	1	2	17	60
B3	10-24	6.0	38	31	31	0.7	0.3	0.3	5.2	15.8	22.3	23.3	3	1	1	23	72
Bca	24-26	7.9	55	25	20	0.0	0.3	0.4	3.7	33.1	37.5	32.6	0	1	1	10	88
C	36+	7.9	66	19	15	0.0	0.4	0.3	2.7	33.4	36.8	28.0	0	1	1	8	90

TABLE VI (h)

ANALYSIS OF A MOUNTAIN PODZOL

Hori- zon	Depth in inches	Mechanical Analysis			Exchangeable cations m.e./100 gm.				Total C.E.C. m.e./100 gm.				% of total C.E.C.			
		%S	%Si	%C	H	Na	K	Mg	Ca	Sum. deter.	H	Na	K	Mg	Ca	
Profile I																
A ₀	0-2	--	--	--	0.3	0.4	1.6	14.1	36.0	52.4	62.3	1	1	3	27	68
A ₂	2-3	29	65	6	0.0	0.3	1.0	17.7	10.1	29.1	17.6	0	1	3	61	35
B ₁	3-5	32	54	14	0.0	0.3	0.5	6.2	21.9	28.9	19.3	0	1	2	22	75
B ₂	5-12	30	57	13	0.0	0.2	0.4	5.3	24.7	30.6	16.0	0	1	1	17	81
B ₃	12-24	41	40	19	0.0	0.2	0.3	4.2	26.6	31.3	15.3	0	1	1	13	85

TABLE VII (a)

AVERAGES OF THE ANALYSES FOR THE ANTLER SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average % Clay	Average Total C.E.C.	Average % of H Na K	of total C.E.C.	Mg Ca
A	.988	0.5	4.8	20	31.9	2 <1 2	11	84
B	1.504	0.1	1.0	26	28.8	1 <1 1	10	87
C	1.709	-	-	28	25.6	0 <1 <1	12	87

TABLE VII (b)

AVERAGES OF THE ANALYSES FOR THE CYGNET SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average % Clay	Average Total C.E.C.	Average % of H Na K	of total C.E.C.	Mg Ca
A1	.957	0.3	4.2	27	31.2	10 <1 4	11	74
B1	1.640	.07	1.1	30	25.3	8 1 2	14	75
B2	1.646	.08	0.7	31	22.4	6 2 2	14	76
B3	1.650	---	---	32	21.9	3 2 2	17	76
Bca	1.722	---	---	27	21.9	0 <1 <1	11	87

TABLE VII (c)

AVERAGES OF THE ANALYSES FOR THE FALUN SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average % Clay	Average Total C.E.C.	Average % of H Na K	Total C.E.C.	Mg Ca
A ₁	.948	.78	3.8	22	31.8	13 1 4	8 74	
A ₂	1.545	.05	0.3	12	10.5	10 2 2	15 71	
B ₁	---	.06	0.4	25	14.9	12 2 2	17 67	
B ₂	1.703	.05	0.5	28	21.5	10 2 2	17 69	
B _{ca}	1.747	---	---	18	18.8	0 1 1	16 82	

TABLE VII (d)

AVERAGES OF THE ANALYSES FOR THE BENALTO SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average		Average % of Total			C.E.C. Ca	
				% Clay	Total C.E.C.	H	Na	K		Mg
All	.620	.66	7.8	18	50.0	8	1	3	8	80
A15	1.265	.16	1.6	18	17.7	9	2	3	9	77
A2	1.376	.10	0.7	17	26.0	8	2	3	12	75
B2	1.656	.06	0.5	16	25.2	7	2	2	18	71
B3	1.612	---	---	26	24.3	7	1	1	14	77
Bca	1.728	---	---	24	22.7	0	1	1	8	90

TABLE VII (e)

AVERAGES OF THE ANALYSES FOR THE BRETON SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average % Clay	Average Total C.E.C.	Average % H	Average % Na	Average % K	Total C.E.C. Mg	C.C. Ca
A1	---	1.37	2.1	16	52.6	7	>1	4	8	80
A2	1.432	.05	0.5	9	8.5	19	2	7	18	54
B1	1.725	.05	0.6	29	22.3	5	1	3	17	74
B2	1.811	.05	0.6	32	24.7	10	>1	3	16	70
B3	1.766	---	---	32	22.9	7	1	2	13	77
B _{ca}	1.614	---	---	26	21.1	0	1	1	9	89

TABLE VII (f)

AVERAGES OF THE ANALYSES FOR THE CAROLINE SERIES

Horizon	Volume Weight	% Nitrogen	% Carbon	Average % Clay	Average Total C.E.C.	Average % H	Average % Na	Average % K	Total C.E.C. Mg	C.C. Ca
Ao	---	---	---	14	56.5	3	1	3	16	77
A2p	.914	.08	0.8	10	12.8	17	2	3	16	62
Bp	1.220	.08	0.7	12	14.2	24	2	8	11	55
Cp	1.510	.10	0.3	7	9.3	17	2	7	14	60
B1	1.465	.03	0.4	37	27.2	7	1	3	14	75
B2	1.545	.04	0.4	36	23.1	8	1	2	15	74
B3	1.545	---	---	44	28.1	7	1	4	16	72
B _{ca}	1.572	---	---	29	29.1	0	1	1	12	86

TABLE VII (g)

AVERAGES OF THE ANALYSES FOR THE LOBLEY SERIES

Horizon	% Nitrogen	% Carbon	Average Clay	Average Total C.E.C.	Average % of total C.E.C. H Na K Mg Ca
Ao	---	---	--	54.7	5 1 1 12 82
A2p	.07	0.6	14	9.7	32 4 7 11 46
Bp	.05	0.7	12	13.0	28 3 4 17 48
Cp	.03	0.3	5	9.5	29 2 2 14 53
B2	.04	0.5	30	19.2	15 1 1 18 65
B3	.04	---	31	23.7	6 1 1 19 73
Bca	---	---	30	27.2	0 1 1 11 87

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TABLE VII (h)

DETERMINATION OF CARBON AND NITROGEN IN A MOUNTAIN PODZOL

Horizon	% Nitrogen	% Carbon
Ao	1.19	---
A2	.12	2.23
B1	.07	1.70
B2	.08	1.54
B3	---	---

TABLE VIII

TOTAL FUSION ANALYSIS FOR THE SOIL HORIZONS OF THE DIFFERENT SERIES SAMPLED

Horizon	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂
Antler series Profile I						
A	69.9	2.7	10.9	1.0	0.7	0.9
B	76.9	3.0	12.8	0.6	0.8	0.9
C	65.6	2.5	11.9	7.0	1.6	0.9
Cygnets series Profile I						
A ₁	67.6	3.5	11.5	1.5	1.3	0.9
B ₁	69.8	3.9	11.7	1.4	0.8	0.8
B ₂	74.3	4.1	12.3	1.0	0.8	0.8
B ₃	72.8	4.5	12.9	1.1	0.9	0.9
B _{ca}	67.4	3.8	10.8	5.7	1.0	0.8
Falun series Profile I						
A ₂	78.5	3.1	9.2	0.6	0.7	1.0
B ₁	78.1	3.4	10.0	0.7	0.8	0.9
B ₂	71.6	4.9	12.9	0.9	1.1	1.2
B _{ca}	75.2	3.6	10.7	1.7	1.1	0.8

TABLE VIII

TOTAL FUSION ANALYSIS FOR THE SOIL HORIZONS OF THE DIFFERENT SERIES SAMPLED (cont'd.)

Horizon	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂
		Benalto series		Profile I		
A11	42.5	2.1	7.6	3.0	0.6	0.6
A15	73.0	3.3	12.2	0.9	0.7	0.9
A2	74.1	3.4	12.0	0.9	0.7	0.9
B2	73.7	4.7	12.6	1.1	0.9	0.8
B3	68.9	5.0	14.9	1.4	1.1	1.0
Bca	63.4	4.5	13.0	6.4	1.3	0.8
		Breton series		Profile I		
A1	44.4	1.6	6.6	3.0	0.4	0.7
A2	79.5	2.3	9.9	0.8	0.6	1.0
B1	77.6	3.4	11.0	0.6	0.6	0.9
B2	76.5	3.3	10.8	0.6	0.6	0.9
B3	75.2	3.8	12.1	0.8	0.7	0.9
Bca	67.6	3.8	13.5	3.2	1.1	0.9

TABLE VIII

TOTAL FUSION ANALYSIS FOR THE SOIL HORIZONS OF THE DIFFERENT SERIES SAMPLED (cont'd.)

Horizon	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂
Caroline series Profile I						
A ₂ p	73.4	2.2	10.9	0.8	0.4	1.0
B _p	70.8	3.2	16.0	0.7	0.5	1.0
C _p	80.1	2.4	10.7	0.5	0.4	1.0
B ₁	73.7	3.6	12.9	0.5	0.7	1.0
B ₂	72.5	3.9	13.9	0.9	0.8	0.9
B ₃	71.8	3.9	15.3	1.0	0.9	1.0
B _{ca}	70.3	4.3	15.4	1.0	1.0	1.0
Lobley series Profile III						
A ₂ p	77.3	1.8	11.3	1.3	1.6	0.6
B _p	76.3	3.3	11.5	0.8	0.9	0.7
C _p	79.9	2.7	10.2	0.5	0.7	0.7
B ₂	71.1	4.6	13.1	0.8	1.1	0.7
B ₃	71.9	4.6	13.6	1.3	1.4	0.6
B _{ca}	68.4	3.8	11.4	5.4	1.9	0.5

TABLE VIII

TOTAL FUSION ANALYSIS FOR THE SOIL HORIZONS OF THE DIFFERENT SERIES SAMPLED (cont'd.)

Horizon	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂
Mountain podzol						
A ₀	25.3	1.8	4.7	6.6	2.2	0.4
A ₂	57.7	3.5	9.8	5.7	1.6	0.8
B ₁	69.6	4.4	13.6	1.4	1.2	1.0
B ₂	68.3	4.9	12.6	1.5	1.6	1.0

TABLE IX

SEMIQUANTITATIVE X-RAY SPECTROGRAPH ANALYSIS OF CLAY FRACTIONS
OBTAINED FROM CAROLINE PROFILE III

Sample	Montmor- illonite	Chlor- ite	Illite	Kaolinite	Amorphous material	230A	Quartz	Remarks
A _{2p} untreated	-	-	minor	minor	dominant- major	-	17%	Mixed layer- ing in illite.
treated with H ₂ O ₂ + HCl	major	minor	minor	trace	-	-	10%	
B _p untreated	-	dominant to major	trace ?	?	?	-	12%	Chlorite broad.
treated with H ₂ O ₂ + HCl	-	minor	trace	-	major- minor	trace	10%	
C _p untreated	minor	-	major	major- minor	-	-	24%	Montmor- illonite mixed layer
treated with H ₂ O ₂ + HCl	minor	-	major	major.	-	minor	17%	Montmor- illonite mixed layer
B ₂ untreated	major- minor	trace ?	major- minor	minor	-	-	22%	Montmor- illonite mixed layer

TABLE X

TOTAL FUSION ANALYSIS ON THE CLAY FRACTIONS FROM CAROLINE PROFILE III
OBTAINED FROM THE SOILS TREATED AND UNTREATED WITH H₂O₂ + HCl FOR THE
MECHANICAL ANALYSIS PROCEDURE

Sample	SiO ₂	Total fusion analysis on the clay				size MgO	TiO ₂	Mechanical Analysis		
		Fe ₂ O ₃	Al ₂ O ₃	CaO				Sand	Silt	Clay
A _{2p}	untreated	59.7	3.4	14.7	.8	.8	1.3	27	70	3
	treated	56.6	4.5	17.9	.9	1.2	1.3	25	63	12
B _p	untreated	50.6	7.1	23.0	1.1	1.4	1.3	21	74	5
	treated	47.2	7.6	24.9	.9	1.4	1.1	20	65	15
C _p	untreated	59.3	6.8	15.6	.7	1.8	1.3	17	80	3
	treated	55.7	7.4	13.4	.7	1.8	1.4	17	78	5
B ₂	untreated	58.6	7.9	18.6	.8	2.0	1.2	4	70	26

DISCUSSION OF RESULTS

Tables VI (a-h) show a marked uniformity in composition for the profiles of each series. There would be little difficulty in placing the different profiles of each series into the proper group by using analytical data alone. However, the Benalto and Falun series, which are both degraded black profiles, and the Caroline and Lobley series which are podzolized grey wooded profiles, differ only in the parent materials from which they were derived.

The total exchange capacity as determined by summation differs from that found by direct determination. The large difference between the total exchange capacity for the B_{ca} and C horizons as determined by summation and distillation may be accounted for by the presence of free Ca CO₃ that is dissolved by the leaching solution and is added to exchangeable calcium. This is in accord with results of other workers (13) who have shown that NH₄Ac solution dissolves CaCO₃ more readily than water does. In other horizons the total exchange capacity found by ammonia determination was consistently lower than that found by summation. This difference is not greater than similar data reported by others (3, 27).

The uniformity of the data for the series suggested averaging results of each of the series. Tables VII (a-h) reflect the distinguishing characteristics of these series as shown by the analyses made. These analyses show a stepwise progression from the normal black earth profile to the podzolized grey wooded profile. These changes are accompanied by a

movement of clays from the upper horizons to the lower horizons and the formation of an ashy-grey A₂ horizon and a well structured B₂ horizon. With encroachment of a coniferous forest, the micro-podzol forms within the A₂ horizon of the grey wooded profile.

The nitrogen content of the soil shows a relationship to the amount of degradation that has taken place. The average percentages of nitrogen for the different series increase near the surface and decrease in the lower horizons as podzolic processes proceed, and as the vegetation changes from grass to forest. This relationship is characteristic of similar soils (17). The organic carbon contents, indicative of organic matter, are closely correlated to nitrogen in these soils.

The percentage of exchangeable cations in the soil is found to vary with the soil series. The most striking relationship exists between the exchangeable cation status of the soil and the amount of podzolic degradation that has taken place in the profile. The largest change was noted in exchangeable calcium, which decreases in the upper horizons of eluviation as soil degradation takes place; on the other hand exchangeable hydrogen increases (with the exception of the mountain podzol). No statistical relationship was found between the amounts of exchangeable calcium and hydrogen. In general, the calcium remains as the dominant exchangeable cation in all horizons and reaches a minimum of approximately

one-half saturation in the more severely eluviated horizons. The podzolic processes have not been severe enough to remove all the exchangeable calcium.

The amounts of exchangeable hydrogen present are reflected by corresponding changes in the pH's of these soils. The decrease in pH of the A and B horizons as podzolization continues, would indicate that the soil solutions are increasing in acidity as podzolization proceeds. Since hydrogen can compete more favourably for the exchange positions under increased acidity, a gradual increase in percentage exchangeable hydrogen is to be expected. The pH of these soils reaches a minimum in the B horizon and as degradation proceeds this lower pH becomes more obvious. This is contrary to what is expected since the A₂ has the higher percentage of exchangeable hydrogen. The humic layer has the lowest pH in a true podzol and the B₁ and B₂ may be its counterpart in the grey wooded soils. It is typical of Alberta soils of a podzolic nature that lowest pH's occur in the B₁ or B₂ horizon (4, 23).

The proportions of some metallic cations increase with degradation. The percentage of exchangeable magnesium remains fairly constant or increases slightly, while the percentage of exchangeable sodium and to a much greater extent exchangeable potassium increase in the eluviated horizons. This is contrary to what is expected since sodium, potassium, and magnesium are all more easily displaced from the exchange complex under the conditions existing in the soil and should

be leached downward more rapidly than Ca. According to Lyon and Buckman (17) the breakdown of primary minerals resulting in clay genesis is accompanied by a release of potassium, sodium, and magnesium which could then become exchangeable cations. They also state that changing of illite by recrystallization to form montmorillonite under acidic conditions, is accompanied by a considerable release of potassium which could replace other exchangeable cations. This may explain why exchangeable sodium is ordinarily present in lesser amounts than exchangeable potassium in the upper horizons.

The total cation exchange capacity is related to clay content. This was tested statistically and it was found that $r = .705$ for 38 degrees of freedom. Values of r for 5% and 1% points are .325 and .418 respectively. The relationship is significant beyond the 1% level and is therefore highly significant. Such a relationship is to be expected since the low organic matter content results in the exchange complex being primarily clay.

The volume weights of the soil vary for the different horizons. Lyon and Buckman (17) state that volume weight is a good indication of soil compaction and structure, and that downward movement of clays may also give rise to dense layers of high volume weight. The B_{ca} horizon, lacking structure, and being compressed by the upper horizons has the highest volume weight and low porosity. Even though the B_2 horizon has root penetration and good structure, the movement

of clays from the horizons of eluviation result in low porosity and the second highest volume weight.

Clay contents vary with soil horizons especially in the more strongly podzolized profiles. Considering the differences in the percentage clay for the B₂ and B_{ca} horizons in most of the profiles it is difficult to conceive that they are solely due to eluviation. Perhaps weathering of primary minerals in the sand fraction and probably to a greater extent in the silt fraction gives rise to additional clay in the B₂ horizon. The fact that the B₂ horizon has the more acidic pH should be conducive to a greater rate of weathering and increase in clay. Other workers (1) have shown that actual formation of clays does take place by the weathering of primary minerals in the soil profile.

The data of Table VIII are in sharp contrast to those of Tables VI (a-h). The soil horizons are not reflected by these data, with the exception of the Caroline profile. The podzolized horizons of that series do increase in sesquioxides to some extent. The stepwise relationship to soil degradation as found in Tables VI (a-h) is lacking. It would be difficult to distinguish the soil series from each other on the basis of the total fusion analysis alone.

A relationship exists between the percentage Al₂O₃ and the clay content of the soils. In most cases fairly large increases and decreases in the clay content are accompanied by relatively small increases and decreases in the

percentage Al_2O_3 . The significance of this relationship was tested for statistically and it was found that $r = .59$ for 38 degrees of freedom. Values of r for 5% and 1% points are .325 and .418 respectively. The relationship is therefore significant beyond the 1% level; however, this relationship is not very obvious by visual observation because of the relatively small differences in percent Al_2O_3 between the soil horizons. Aluminum is one of the major constituents of clay minerals and such a relationship is to be expected. This relationship is not directly proportional since there is a variation in the types of clay in the different horizons and they differ in their Al_2O_3 content. Under acid weathering hydrous micas such as illite change to montmorillonite which upon further acid weathering change to kaolinite as suggested by the data in Table IX. This relationship has been shown to be true by other workers (17). Another reason for the Al_2O_3 content not being directly proportional to the clay content may be that some material less than 2 microns in size, is amorphous material, such as silica and quartz. In Table IX the quartz contained in the C_p and the B_2 horizons less than 1 micron in size is almost twice that in the A_{2p} and B_2 horizons. Since a relationship does exist between the clay content and the percent Al_2O_3 , variations are to be expected in the percentage Al_2O_3 for similar profiles varying only in texture.

The analyses by the X-ray spectograph in Table IX substantiate the need for the peroxide and HCl treatment

employed in the modified pipette method for mechanical analysis (36). The large increase in clay content in the two upper horizons, as indicated in Table X, brought about by treatment is probably due to a breakdown of aggregates composed primarily of clay particles. In comparing clays from treated and untreated samples there was no significant difference in the B_p and C_p horizons except for the appearance of a diffraction line at 23⁹Å after standard glycol treatment; however, its appearance is insignificant. The larger percentage of clay in the A_{2p} and B_p horizons compared to the C_p (in the treated samples) is best explained by an active breakdown of silt size particles to form additional clay.

The data of Tables IX and X show that the B_p horizon of the Caroline does have some accumulation of sesquioxides, but their presence is probably only in small concentrations. It is quite obvious that differences in Al₂O₃ and Fe₂O₃ in other horizons may largely be accounted for by the presence of varying amounts of different types of clay rather than the presence of large concentrations of free oxides.

The mountain podzol was very different to other podzolized soils in this region and also to those described in the literature. While the physical appearance of this profile suggests that podzolic processes have been responsible for its development, the analytical data do not confirm this

in anyway. All horizons were found to contain a high percentage of exchangeable magnesium with the higher concentrations near the surface. Exchangeable hydrogen was very low. $\text{Mg}(\text{HCO}_3)_2$, MgCO_3 , and CaCO_3 , were found in all horizons, with CaCO_3 predominating in the lower horizons. Analytical data do not verify the process as being podzolization, and this soil should be distinguished from podzol soils as described in the literature, at least until such time as the exact nature of the profile development is established.

Among the analyses carried out, the pH and the exchangeable cation status show most clearly that there are definite differences between the soil series studied. Similar data were reported by Ulrich (38) who studied the chemical changes in prairie, Wiesenboden, and planosol soils developed on Peorian loess. Increased horizon differentiation was accompanied by a progressive removal of exchangeable calcium from the profile and an increase in hydrogen. Exchangeable magnesium showed a tendency to persist longer than calcium in exchangeable form. It was shown that exchangeable potassium decreased rather than increased during maximum eluviation while sodium increased and was retained at a higher level in exchangeable form than potassium. The pH also decreased with sharper horizon differentiation. A study of solonetzic soils by Bentley and Rost (3) indicated similar trends in pH and exchangeable H as horizon differentiation continued. In all cases the resultant profiles had an eluviated ashy grey silicious A_2 horizon and a well developed fairly heavy textured

illuvial B horizon. The two pedogenic processes mentioned above are entirely different from the podzolization process; however, all three processes involve movement of clays from the A to the B horizons and definite changes in the cation exchange status in each of the profiles as development proceeds. The morphological features resulting from the three pedogenic processes are distinguishable in the field.

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APPENDIX

SECTION I

Determination of Calcium and Magnesium by Versene

A. Preparation of Reagents

1. Standard calcium solution

Weigh out 5.00 grams of reagent grade calcium carbonate and dissolve with 45.0 ml. of 1:1 HCl (which is the minimum amount necessary to ensure solution).

After solution make up to 1000 ml.

This solution is a 0.1N solution.

1 cc. of this solution contains 0.1 m.e. of calcium.

2. Standard magnesium solution

Dissolve 12.300 grams $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and make up to one litre. This solution is 0.1N with respect to Mg and 1 cc. contains 0.1 m.e. of Mg.

3. Versene solution

Using Di-sodium versenate (ml. wt. 372.35) from Bersworth Chem. Company, Framingham, Mass. or Eastman Chem. Company, 1.8616 grams per litre will give a solution that is approximately 0.01N for calcium and magnesium.

Standardize versene against exactly 3 ml. portions of calcium solution.

10 cc. of 0.01N versene reacts with 1 cc. of solution containing 0.1 m.e. of calcium.

4. Buffer solution

Dissolve 67.5 grams NH_4Cl in 250 ml. water and mix with 570 ml. NH_4OH . Dilute to one litre. Five millilitres added to approximately 100 ml. gives a pH of 10 to a solution being titrated.

5. F241 (Eriochrome black T) indicator (obtainable from Eastman)

Dissolve 0.2 grams E black T in 50 ml. methyl alcohol containing 2 grams hydroxylamine hydrochloride.

Indicator should not be older than two months in order to obtain a distinct end point.

6. Composite solution

Prepare 100 ml. of 5% hydroxylamine hydrochloride. Prepare 100 ml. of 2% KCN. Mix these two solutions adding 10 ml. of .1N Mg standard. Make volume up to 250 ml. This solution should be kept tightly stoppered and should be used fresh (not over one day old). Five ml. of this solution (measured accurately) is added to each unknown for versene titration, and is also taken for each blank. (The magnesium in the solution serves the purposes of a positive blank).

7. Acidic 3% NH_4Cl

Prepare a convenient amount of a solution containing 3% NH_4Cl and 10% dilute HCl.

8. Two per cent $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution.

9. Methyl red indicator.

10. Standardized KMnO_4 solution approximately .05N.

B. Details of the Determinations

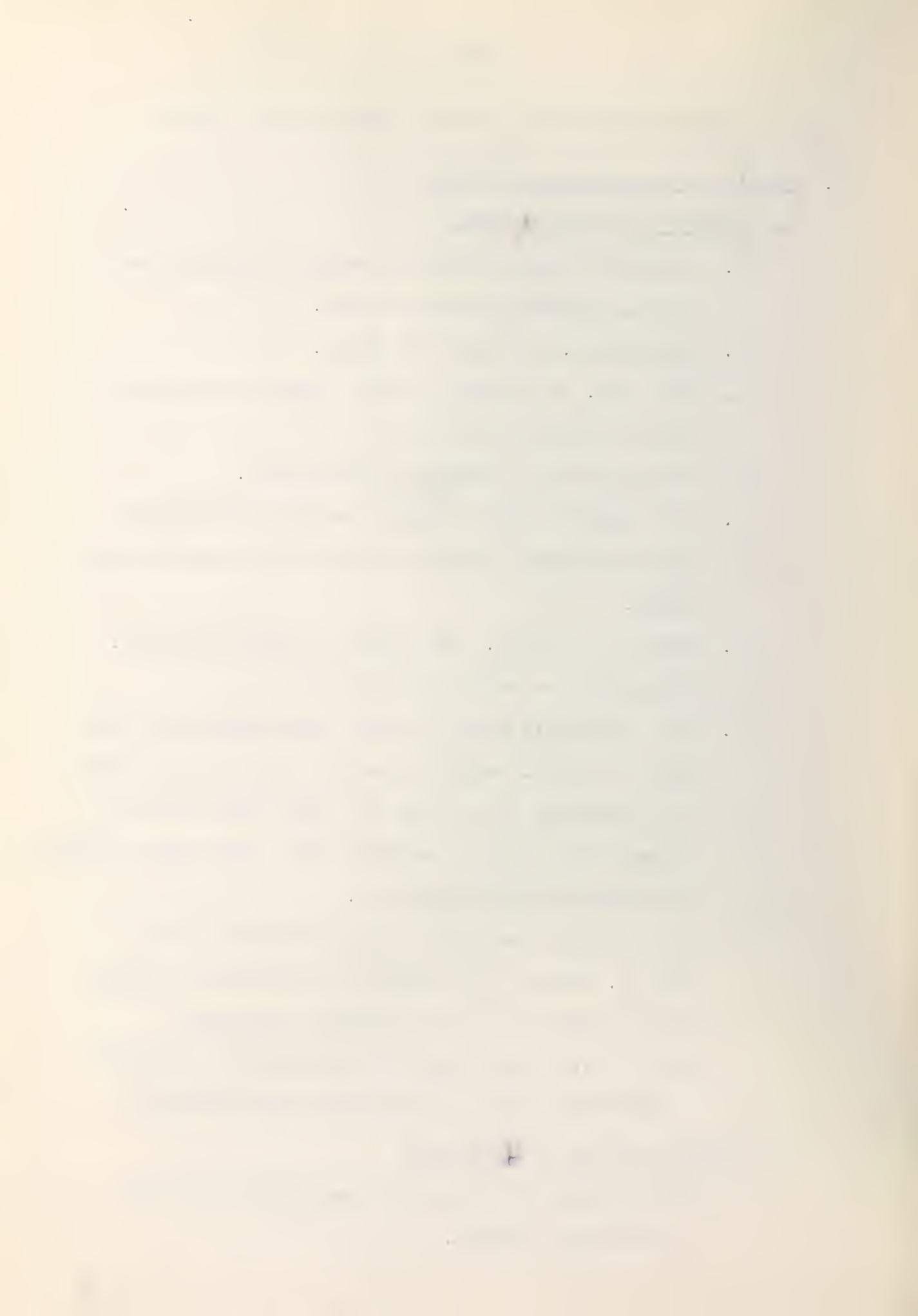
1. Determination of calcium

- a. Transfer 5 ml. of unknown extract from soil to a 50 ml. pointed centrifuge tube.
- b. Add one ml. of acidic 3% NH_4Cl .
- c. Add 5 ml. of 2% $(\text{NH}_4)_2 \text{C}_2\text{O}_4$ solution and water to give a volume of 30-35 ml.
- d. Add one drop of methyl red indicator.
- e. Add dropwise with constant swirling 1:20 NH_4OH until one drop changes indicator to a yellow basic color.
- f. Make up to 50 ml. and allow to stand 1.5 hours.
- g. Centrifuge to settle precipitate.
- h. Very carefully decant liquid from centrifuge tube into a 250 ml. beaker allowing tube to drain well (and removing final drop of liquid from tube by touching lip tip to beaker wall). Save this solution for magnesium determination.
- i. Wash CaC_2O_4 precipitate quantitatively into a 250 ml. beaker, and add 5 ml. concentrated H_2SO_4 , heat to above 60°C and titrate with KMnO_4 .

No. of m.e. of calcium in the aliquot analyzed =
Normality x ml. of titer used for titration.

2. Determination of magnesium

- a. Make volume of decantate from centrifuge tube up to about 100 ml.



- b. Add 5 ml. of composite solution.
- c. Add 5 ml. of buffer solution.
- d. Add about 10 drops of E black T indicator.
- e. Titrate with versene to the end point of indicator (when last tint of purple disappears and solution is only blue). This titration is matched to a blank.

No. of m.e. of magnesium in aliquot analyzed =
 normality of versene x (cc. used for titration - blank).

C. Recovery of Calcium and Magnesium Added to Unknown NH₄Ac Extracts

<u>Solution</u>	<u>Ca, m.e. in solution</u>	<u>Mg, m.e. in solution</u>	<u>Total Ca and Mg, m.e. in solution</u>
unknown 1.	41.5	8.3	49.8
unknown + Ca + Mg	51.3	17.0	68.3
added Ca + Mg	9.8	8.7	18.5
recovery, unknown 1.	9.8	8.7	49.8
unknown 2	41.6	8.0	49.6
unknown 2 + Ca + Mg	51.3	16.8	68.1
added Ca + Mg	9.8	8.7	18.5
recovery unknown 2	9.7	8.8	49.6

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